



Ag–M (M: Ni, Co, Cu, Fe) bimetal catalysts prepared by galvanic deposition method for CO oxidation



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ABSTRACT

Ag–M (M: Fe, Co, Ni, Cu) bimetal catalysts supported on SiO₂ were prepared by galvanic deposition (GD) method. HAADF-STEM observation and EDX elemental mapping showed that Ag was successfully introduced on Fe, Co, Ni, and Cu particles using the GD method. Ag–Fe, Ag–Co, and Ag–Cu catalysts showed Janus structure that is Ag nanoparticles (NPs) on the 3d metals. On the other hand, Ag–Ni catalyst showed core–shell like structure composed of small Ag NPs (<10 nm) or thin layer on Ni particles. The catalytic activities of Ag–M bimetal catalysts were evaluated by CO oxidation reaction. All Ag–M bimetal catalysts showed higher catalytic activities than Fe, Co, Ni, Cu, and Ag mono-metal catalysts. In particular, Ag–Ni bimetal catalyst having core–shell like structure showed remarkable enhancement of the catalytic activity.

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1. Introduction

Platinum-group metals (PGMs) are essential components of catalysts for various industrial processes including petroleum chemistry, synthesis of fine chemicals, and purification of exhaust gases from plant and automobile [1–3]. However, PGMs are expensive and scarce resources. Therefore, alternatives to PGM catalysts are increasingly required.

To design PGM-free catalysts, the d-band theory by Nørskov et al. is useful, because the theory provides a correlation between the d-band center of transition metal surfaces and its catalytic activity [4,5]. For example, catalytic activity for oxygen reduction reaction shows a volcano-type dependency on the d-band-center of the metal catalysts [6]. Thus, the first step to design the PGM-free catalysts as alternatives of the PGM ones is to investigate the correlation between the catalytic activity of the PGM-free catalysts and their modification which will cause the shift of the d-band center. Bimetalization is one of the strategies to control the d-band-center of catalyst surface [5,7–9]. It has been reported that the

d-band-center of bimetal catalysts could be changed by the ligand effect and strain effect [8,10,11]. In general, d-bands of coinage metals such as Ag reside below the Fermi level in a bulk state [12], and their bulk metals are usually catalytically poor (except for ethylene oxidation in the case of Ag [13]). On the other hand, d-bands of 3d transition metals such as Fe, Co, Ni, and Cu reside above the Fermi level and the position of their d-band center is in order [5]. The combination of the coinage metals with the above 3d metals may lead to the gradual shift of the d-band center and change the catalytic activity according to their shift.

Preparation methods of bimetal catalysts have been developed [14]. A galvanic deposition (GD) method is one of the preparation methods of bimetal catalysts [15–17]. In a GD process, a supported metal X is replaced by another metal Y precursor having lower ionization tendency through galvanic reaction. Recently, we have prepared SiO₂ supported Ag–Ni bimetal catalysts using a GD method [18]. The AgNi catalysts showed higher catalytic activity for CO oxidation than Ag and AgNi catalysts prepared by a conventional impregnation method. In the present study, bimetal catalysts of Ag and various 3d transition metals (Fe, Co, Ni, and Cu) were prepared by a GD method, and their catalytic activity for CO oxidation reaction was evaluated to investigate the effect of bimetalization of Ag and 3d transition metals.

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Table 1
The features of catalysts prepared. All catalysts supported on SiO₂.

Catalyst	Preparation method	Reduction temperature for GD method ^a	Metal loadings (wt%) ^b
Fe-I	Impregnation method	–	Fe = 5.0
Co-I	Impregnation method	–	Co = 5.0
Ni-I	Impregnation method	–	Ni = 5.0
Cu-I	Impregnation method	–	Cu = 5.0
AgFe-GD	GD method	600	Ag = 1.5, Fe = 4.7 ^b
AgCo-GD	GD method	500	Ag = 2.9, Co = 4.4 ^b
AgNi-GD	GD method	400	Ag = 0.3, Ni = 3.0 ^b
AgCu-GD	GD method	300	Ag = 2.3, Cu = 4.9 ^b

^a Reduction temperature at which 3d transition elements are completely reduced to metal state was decided using H₂-TPR.

^b Metal loading was measured by ICP analysis.

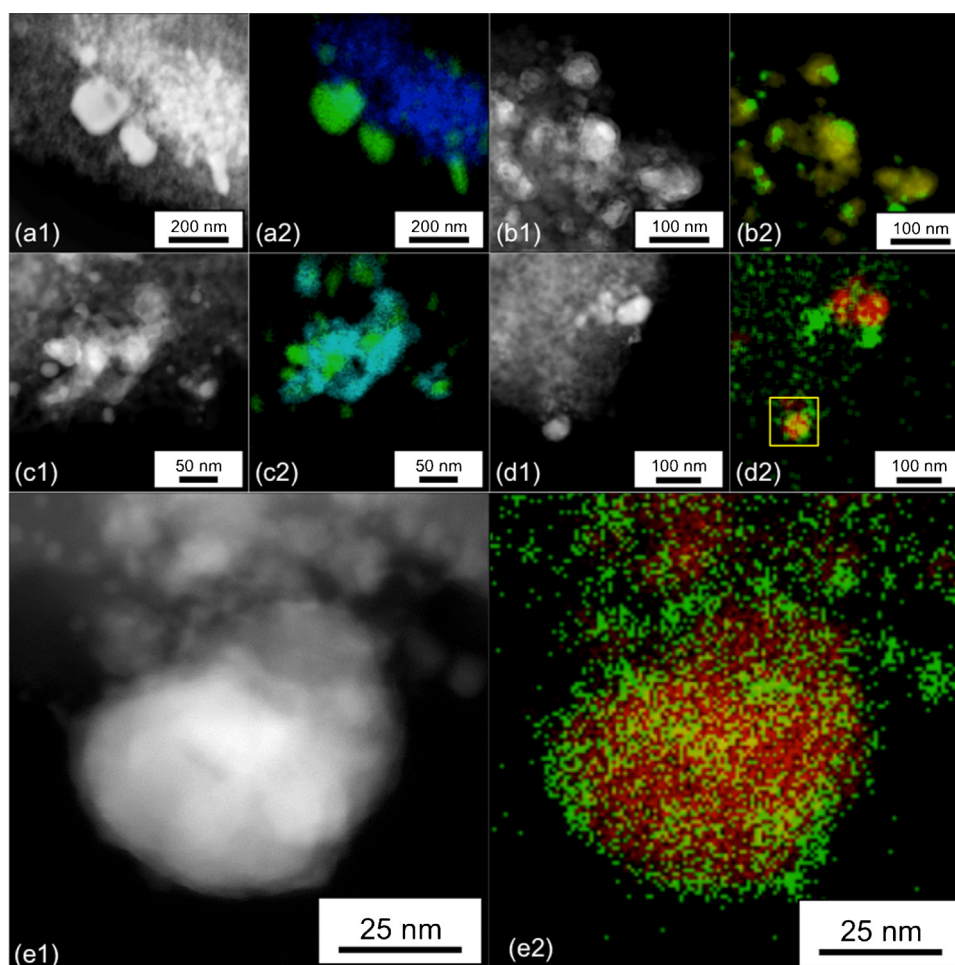


Fig. 1. HAADF-STEM image and EDX elements mapping of AgCo-GD (a1, a2), AgFe-GD (b1, b2), AgCu-GD (c1, c2) and AgNi-GD (d1, d2). (e1, e2) are enlarged images of yellow square of (d2). The green, blue, yellow, cyan, and red colors in EDX mapping correspond to Ag, Co, Fe, Cu, and Ni elements respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Catalysts preparation

AgNO₃, Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O as the metal precursor were purchased by Kishida Chemicals (99.8%, pure). SiO₂ (JRC-SIO-5) as a support was supplied from the Catalysis Society of Japan.

Ni/SiO₂ with 5 wt% of Ni loading was prepared by a conventional impregnation method. Silica as a support was added to aqueous solution of Ni(NO₃)₂, and the mixture was stirred. After evaporating and drying overnight at 80 °C, the resulting solid was calcined at 500 °C for 3 h. Fe/SiO₂, Co/SiO₂, and Cu/SiO₂ (5 wt% of metal loading)

were also prepared in a similar manner (denoted as Fe-I, Co-I, Ni-I, Cu-I, respectively).

Galvanic deposition (GD) method was carried as reported previously [18]. We added Ni/SiO₂ to two-neck round-bottom flask, and capped by a septum. Ni/SiO₂ was reduced under a flow of H₂ at 400 °C for 30 min. After N₂ substitution, the two-neck round-bottom flask with Ni catalyst was cooled with dry ice below –60 °C. We added ethanol into the flask, and dropped the aqueous AgNO₃ solution in ethanol into the flask for 1 h. The obtained solid was centrifuged and dried overnight at 80 °C. The obtained AgNi bimetal catalyst was denoted as AgNi-GD. AgFe, AgCo, and AgCu bimetal catalysts were similarly prepared by GD method (denoted as AgFe-GD, AgCo-GD, and AgCu-GD, respectively). Fe/SiO₂, Co/SiO₂, and

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